Manual of PEARLNEQ
(VERSION COMPATIBLE WITH FOCUS PEARL 3.3.3)

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Tip: Start with the default example, provided with the package!!!

Release notes:
- **Values in table 6 of the PEARL manual should be replaced by the values in this example (see appendix).**
- **The previous version contained a series of small bugs. These bugs have been fixed in this version.**
- **The weighing factors for the measurements have changed: all measurements are now given a weighing factor that equals the inverse of each measured value, thus giving equal weight to all measurements.**
- **According to recommendations of the FOCUS Kinetics Workgroup, the initial mass in the system should be optimised. This recommendation has been implemented in the current version.**
- **A second example (example2.mkn) has been added.**

This document describes the PEARLNEQ-PEST combination, which can be used to obtain the half-life at reference temperature (DT50Ref), the desorption rate coefficient (CofRatDes), and the multiplication factor for the non-equilibrium sorption coefficient (FacSorNeqEql) in the case of sorption/desorption kinetics. If the incubation experiment has been carried out at multiple temperatures, the molar activation energy (MolEntTra) can be optimised simultaneously.

Precautionary remark

This PEARLNEQ software tool should be seen as an introduction to fitting results experiments on long-term sorption kinetics to the PEARL sorption submodel. PEARLNEQ shows you how PEST can be coupled to a fortran programme that contains this PEARL sorption submodel (i.e. PEARLNEQ.EXE). PEARLNEQ should not be seen as a ready-to-use tool. PEARLNEQ provides you with example input files to the PEST optimisation package and shows you how to organise this optimisation. We had to make a number of assumptions for generating these PEST input files (e.g. upper and lower bounds of parameters, weighing factors for each measurement, etc. etc.). We do not claim that these assumptions are defensible for your problem; they are our best guesses at this moment.

While using PEARLNEQ, we noticed that very regularly the results depend on the initial guesses of the parameters. Therefore we advise you to perform always a

number of runs with different initial guesses. We advise you also to analyse the results very carefully (especially the confidence intervals of the estimated parameters). We do not accept any responsibility for use of PEARLNEQ.

Running the example

The following steps must be followed.

1 **Installation.** PEARLNEQ is distributed in a self-extracting zip file. Run unpack_pearlneq.exe and specify a path (e.g. c:\pearlneq). The package contains three directories, i.e. Neq_Bin, pest and Neq_Example.
   - The Neq_Bin directory contains the PEARLNEQ executables, PEARLNEQ.EXE and PEARLMK.EXE.
   - The PEST optimisation software is available in the pest directory. As PEST is now available freeware (http://www.sspa.com/pest), we included the latest version as of 29-10-2003 (version 7.0.1.). Separate installation of PEST is not necessary.
   - The Neq_Example directory contains results from an example study, as described in the PEARL user manual, page 51-54.

2 You can now run the example, to check if everything works and get experience with the system. Go to the Neq_Example directory, and run the example, example.bat.
   - The batch file will first call PEARLMK. This pre-processing program generates the input files for PEST, i.e. example.pst, example.tpl and example.ins.
   - Than the optimisation starts. PEST calls PEARLNEQ several times (in the example 39 times).
   - If you get an error message after the first step (PEARLMK), type control-break to stop the process and check the error messages available in the example.err file.

3 After successful optimisation, read the results from the file example.rec. The relevant results, including parameter values, 95% confidence intervals and correlation matrices can be found at the end of this file. PEST also generates parameter sensitivity files etc. Details can be found in the PEST manual, which is available in the PEST subdirectory of the package.

4 If you encounter errors during the second step, you can try running PEARLNEQ directly. PEARLMK has created a file example.neq, which is the input file for PEARLNEQ. Type ..\Neq_Bin\PEARLNEQ EXAMPLE. PEARLNEQ will create an output file (example.out) and a log file (example.log). The output files are self-explaining.

5 You can use the XyWin program to make a graph. XyWin is available in the neq_bin\xypearl directory of PEARLNEQ (the example job does this call for your):

```
..\Neq_Bin\xypearl\xywin –j example.job –W l
```

Run PEARL_Neq with your own data

1 Be sure that an appropriate incubation experiment has been carried out (see the FOCUS PEARL user manual). The first step of optimising your own data consists of **editing the file example.mkn**, which can be found in the example subdirectory of the **PEARLNEQ directory**. *Please make a copy of this file before editing.* An example of this input file is listed at the end of this appendix. The following parameters must be provided:

- TimEnd (d): The duration of the incubation experiment.
- MasSol (g): The mass of dry soil incubated in each jar.
- VolLiqSol (mL): Volume of liquid in the moist soil *during* incubation.
- VolLiqAdd (mL): Volume of liquid added to the soil *after* incubation (i.e. the amount of liquid added to perform a conventional desorption equilibrium experiment).
- CntOm ($kg.kg^{-1}$): Mass fraction of organic matter in the soil.
- ConLiqRef ($mg\ L^{-1}$): Reference concentration in the liquid phase.
- ExpFre (-): Freundlich exponent.
- KomEql ($L\ kg^{-1}$): coefficient of equilibrium sorption on organic matter.
- MasIni (µg): The initial total mass of pesticide in each jar. *In contrast to the previous version of PEARLNEQ, this parameter will be optimised. There is no default value for this parameter.*
- FacSorNeqEql (-): factor describing the ratio $K_{F,ne}/K_{F,eq}$. *This parameter will be optimised*, but you have to specify an initial guess here. The default value is 0.5.
- CofRatDes (d^{-1}): the desorption rate coefficient. *This parameter will be optimised*, but you have to specify an initial guess here. The default value is 0.01 d^{-1}.
- DT50Ref (d): the transformation half-life under reference conditions. applying to the equilibrium domain. *This parameter will be optimised*, but you have to specify an initial guess here. As a default value, you can use the 'classical' half-life, which applies to the total soil system (i.e. the equilibrium domain + the non-equilibrium domain).
- TemRefTra (C): The reference temperature, at which the half-life should be known. The default values is 20 ^{o}C.
- MolEntTra ($kJ\ mol^{-1}$): the molar enthalpy of transformation. *This parameter will be optimised if you have carried out the experiment at multiple temperatures; otherwise it is a model-input*. If optimised, you have to specify an initial guess here. The default value is 54 $kJ\ mol^{-1}$.
- table Tem (C): List of temperatures at which the incubation experiment has been carried out. At least two temperatures must be specified.
- table Observations: List of observations. The first column contains the time (d), the second column the temperature, column 3 contains the total mass of pesticide in the system (µg), column 4 contains the concentration of pesticide

(µg L^{-1}) in moist soil (then VolLiqAdd = 0) or in the water phase after a desorption experiment (in which case VolLiqAdd is not zero) and column 5 contains the characters 'OBS'.

2. Repeat step 2-5 in the example. **Please replace "example" everywhere it occurs by the name of the copied input file.**
3. If the optimization is not succesfull, you can try re-running PEARLNEQ with different initial guesses of MasIni, DT50Ref, FacSorNeqEql and CofRatDes.

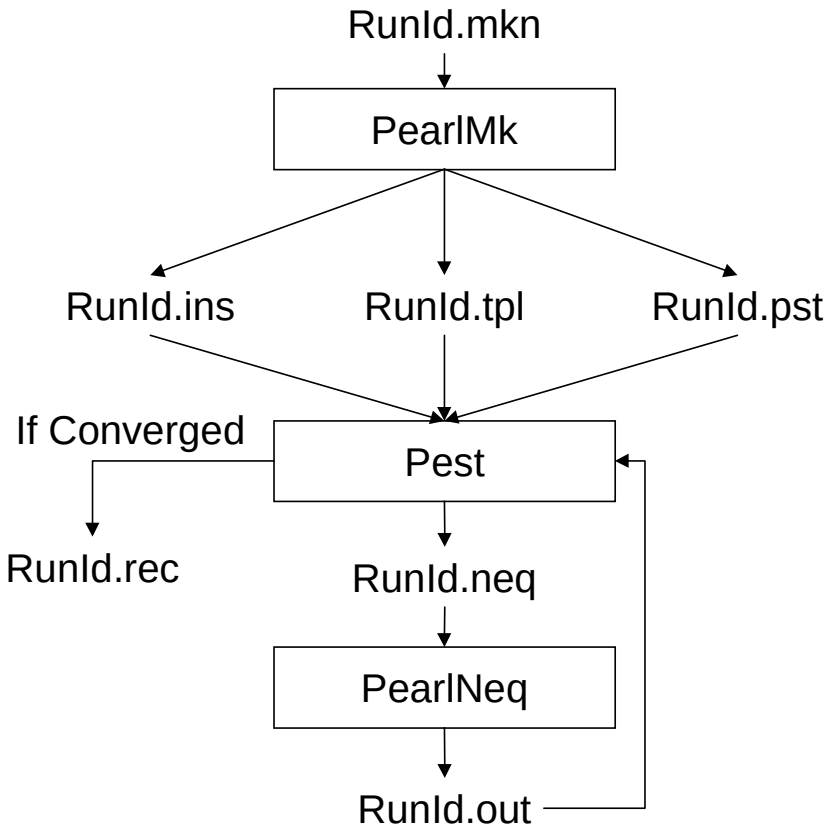

Figure 1 Dataflow diagram for the PEARLNEQ-PEST combination

Example input file

```
*-------------------------------------------------------------------------------------------
* STANDARD FILE for PEARLMK version 3.3.3
* Program to fit the half-life, activation energy and desorption rate in the case of
* pesticide that show kinetic sorption behaviour
*
* This file is intended for use with the PEST program (Doherty et al., 1991).
* Copyright MNP/RIVM/Alterra 2003, 2005, 2006.
*
*-------------------------------------------------------------------------------------------

* Model control
Yes           ScreenOutput
0.0           TimStart       (d)         Start time of experiment
500.0         TimEnd         (d)         Duration of the incubation experiment
0.01          DelTim         (d)         Time step of output

* System characterization
45.36         MasSol         (g)         Mass of soil in the icubation jars
54.64         MasIni         (ug)        Initial guess of the initial mass of pesticide
6.64          VolLiqSol      (mL)        Volume of liquid in the moist soil
0.0           VolLiqAdd      (mL)        Volume of liquid ADDED for equilibrium experiment
0.047         CntOm          (kg.kg-1)   Organic matter content

* Sorption parameter
1.0           ConLiqRef      (mg.L-1)    Reference liquid content
0.87          ExpFre         (-)         Freundlich exponent
2.1           KomEql         (L.kg-1)    Coefficient of equilibrium sorption on org. matter
0.5           FacSorNeqEql   (-)         Initial guess of ratio Kfneq/Kfeql
0.01          CofRatDes      (d-1)       Initial guess of desorption rate coefficient

* Transformation parameters
10.00         DT50Ref        (d)         Initial guess of half-life at reference temperature
20.0          TemRefTra      (C)         Reference temperature
54.0          MolEntTra      (kJ.mol-1)  Initial guess of molar activation energy

* Temperature at which the incubation experiments are being carried out
table Tem (C)
1  5.0
2  15.0
end_table

* Measured mass and concentration of pesticide as a function of time and temperature
* Tim  Tem  Mas       Con
* (d)  (C)  (ug)      (ug/L)
table Observations
2      5    51.6300   5.7285       OBS
10     5    50.5900   5.0560       OBS
42     5    46.0200   3.6635       OBS
87     5    38.6100   2.9320       OBS
157    5    32.8150   1.9280       OBS
244    5    25.8700   1.4650       OBS
358    5    20.3150   0.8820       OBS
451    5     9.4250   0.6015       OBS
2     15    51.3300   5.8955       OBS
6     15    47.3950   4.4425       OBS
10    15    45.0650   3.9510       OBS
42    15    23.1400   1.6470       OBS
87    15    10.8950   0.6710       OBS
157   15     3.1350   0.1525       OBS
244   15     1.4400   0.0305       OBS
358   15     0.4500   0.0000       OBS
451   15     0.1500   0.0000       OBS
end_table
```

Appendix

Results (last section of rec file)

These are the results of the default example, provided with the package.

OPTIMISATION RESULTS

Parameters ----->

Parameter	Estimated value	95% percent confidence limits lower limit	upper limit
fsne	0.600286	0.408681	0.791892
crd	1.226317E-02	9.886449E-03	1.463989E-02
dt50	13.0062	11.5100	14.5024
masini	56.0664	52.1243	60.0084
met	108.755	102.806	114.705

Note: confidence limits provide only an indication of parameter uncertainty.
They rely on a linearity assumption which may not extend as far in
parameter space as the confidence limits themselves - see PEST manual.

See file EXAMPLE.SEN for parameter sensitivities.

Observations ----->

Observation	Measured value	Calculated value	Residual	Weight	Group
o1	51.6300	55.5316	-3.90156	1.9000E-02	no_name
o2	5.72850	5.39742	0.331082	0.1750	no_name
o3	50.5900	53.4684	-2.87844	2.0000E-02	no_name
o4	5.05600	5.08081	-2.480823E-02	0.1980	no_name
o5	46.0200	46.2635	-0.243511	2.2000E-02	no_name
o6	3.66350	4.06320	-0.399703	0.2730	no_name
o7	38.6100	38.2669	0.343149	2.6000E-02	no_name
o8	2.93200	3.09390	-0.161897	0.3410	no_name
o9	32.8150	29.0458	3.76922	3.0000E-02	no_name
o10	1.92800	2.16483	-0.236828	0.5190	no_name
o11	25.8700	20.9646	4.90536	3.9000E-02	no_name
o12	1.46500	1.47675	-1.175005E-02	0.6830	no_name
o13	20.3150	13.8380	6.47702	4.9000E-02	no_name
o14	0.882000	0.932184	-5.018437E-02	1.134	no_name
o15	9.42500	9.90684	-0.481840	0.1060	no_name
o16	0.601500	0.648450	-4.694962E-02	1.663	no_name
o17	51.3300	53.3843	-2.05426	1.9000E-02	no_name
o18	5.89550	5.17830	0.717199	0.1700	no_name
o19	47.3950	48.4369	-1.04190	2.1000E-02	no_name
o20	4.44250	4.62304	-0.180537	0.2250	no_name
o21	45.0650	43.9959	1.06909	2.2000E-02	no_name
o22	3.95100	4.12910	-0.178099	0.2530	no_name
o23	23.1400	21.3140	1.82600	4.3000E-02	no_name
o24	1.64700	1.70735	-6.034768E-02	0.6070	no_name
o25	10.8950	8.98367	1.91133	9.2000E-02	no_name
o26	0.671000	0.544736	0.126264	1.490	no_name
o27	3.13500	3.26320	-0.128203	0.3190	no_name
o28	0.152500	0.131795	2.070505E-02	6.557	no_name
o29	1.44000	1.24259	0.197406	0.6940	no_name
o30	3.050000E-02	3.866613E-02	-8.166130E-03	32.79	no_name
o31	0.450000	0.399623	5.037676E-02	2.222	no_name
o32	0.00000	1.077987E-02	-1.077987E-02	1.000	no_name
o33	0.150000	0.162574	-1.257429E-02	6.667	no_name
o34	0.00000	4.019330E-03	-4.019330E-03	1.000	no_name

See file EXAMPLE.RES for more details of residuals in graph-ready format.

See file EXAMPLE.SEO for composite observation sensitivities.

Objective function ----->

Sum of squared weighted residuals (ie phi) = 0.4297

Correlation Coefficient ----->

Correlation coefficient = 0.8997

Analysis of residuals ----->

All residuals:-

Number of residuals with non-zero weight	= 34
Mean value of non-zero weighted residuals	= 1.3161E-02
Maximum weighted residual [observation "o13"]	= 0.3174
Minimum weighted residual [observation "o30"]	= -0.2677
Standard variance of weighted residuals	= 1.4816E-02
Standard error of weighted residuals	= 0.1217

Note: the above variance was obtained by dividing the objective function by the number of system degrees of freedom (ie. number of observations with non-zero weight plus number of prior information articles with non-zero weight minus the number of adjustable parameters.) If the degrees of freedom is negative the divisor becomes the number of observations with non-zero weight plus the number of prior information items with non-zero weight.

Parameter covariance matrix ----->

	fsne	crd	dt50	masini	met
fsne	8.7787E-03	8.4444E-05	-5.6502E-02	6.4073E-02	0.1016
crd	8.4444E-05	1.3507E-06	-4.5078E-04	6.0200E-04	6.0023E-04
dt50	-5.6502E-02	-4.5078E-04	0.5353	-0.5756	-1.463
masini	6.4073E-02	6.0200E-04	-0.5756	3.716	-0.8663
met	0.1016	6.0023E-04	-1.463	-0.8663	8.463

Parameter correlation coefficient matrix ----->

	fsne	crd	dt50	masini	met
fsne	1.000	0.7755	-0.8242	0.3548	0.3727
crd	0.7755	1.000	-0.5301	0.2687	0.1775
dt50	-0.8242	-0.5301	1.000	-0.4081	-0.6872
masini	0.3548	0.2687	-0.4081	1.000	-0.1545
met	0.3727	0.1775	-0.6872	-0.1545	1.000

Normalized eigenvectors of parameter covariance matrix ----->

	Vector_1	Vector_2	Vector_3	Vector_4	Vector_5
fsne	1.4335E-02	-0.9842	0.1744	-2.2879E-02	1.1198E-02
crd	-0.9999	-1.4279E-02	1.5744E-03	-1.9999E-04	6.4642E-05
dt50	9.4905E-04	-0.1745	-0.9453	0.2229	-0.1618
masini	7.8350E-05	-1.4702E-02	-0.2006	-0.9685	-0.1467
met	7.0894E-05	-1.9859E-02	-0.1889	-0.1084	0.9758

Eigenvalues ----->

4.7821E-07	1.7663E-03	0.1313	3.753	8.837